

# Graphite intercalation compounds under pressure

Gábor Csányi\*,<sup>1</sup> Chris J. Pickard,<sup>2</sup> B. D. Simons,<sup>1</sup> and R. J. Needs<sup>1</sup>

<sup>1</sup>*Theory of Condensed Matter Group, Cavendish Laboratory, University of Cambridge,  
J. J. Thomson Avenue, Cambridge CB3 0HE, United Kingdom*

<sup>2</sup>*School of Physics and Astronomy, University of St Andrews,  
North Haugh, St Andrews KY16 9SS, United Kingdom*

Motivated by recent experimental work, we use first-principles density functional theory methods to conduct an extensive search for low enthalpy structures of  $C_6Ca$  under pressure. As well as a range of buckled structures, which are energetically competitive over an intermediate range of pressures, we show that the high pressure system ( $\gtrsim 18$  GPa) is unstable towards the formation of a novel class of layered structures, with the most stable compound involving carbon sheets containing five- and eight-membered rings. As well as discussing the energetics of the different classes of low enthalpy structures, we comment on the electronic structure of the high pressure compound and its implications for superconductivity.

PACS numbers: 61.66.Fn, 71.15.Nc

Although the history of graphite intercalation compounds (GICs) dates back more than a century, they first became prominent in the early '60s when superconductivity was discovered in some alkali metal GICs [1]. Interest in these compounds has been reignited by the recent discovery that at least two compounds,  $C_6Ca$  and  $C_6Yb$ , have superconducting transition temperatures that, although modest by the standard of cuprate compounds, are an order of magnitude higher than those found previously for GICs [2, 3]. Soon after this discovery, electronic structure calculations revealed that a three-dimensional band, originating from the intrinsic *interlayer* band of graphite and a metal ion band of the intercalant, plays a crucial role in facilitating superconductivity in GICs [4] (see also Ref. [5]). Subsequently, first-principles calculations for  $C_6Ca$  and  $C_6Yb$  [6, 7] provided evidence that the out-of-plane phonons of the graphene sheets and the in-plane phonons of the metal atom couple to the electrons in this three-dimensional band and provide a basis for understanding the superconductivity within a conventional BCS framework. A brief review of the work to date is given in Ref. [8].

As well as superconductivity, evidence for a reversible pressure-driven phase transition has been reported in both  $C_6Ca$  and  $C_6Yb$  [9, 10]. As the pressure is increased from ambient, the superconducting transition temperature increases markedly, rising in  $C_6Ca$  from 11.5 K to 15 K at 7 GPa above which it drops abruptly to 5 K. Similar behaviour is reported in  $C_6Yb$  with a transition at ca. 2.2 GPa. Since the transition is reversible, and calculations have shown softening of a phonon mode with increasing pressure, it was conjectured that a structural phase transition takes place [11, 12]. The reversible na-

ture of the observed transitions suggest that they involve small atomic displacements [22]. However, the various observations motivate an investigation of the wider landscape of structures of GICs under pressure, including the possibility of large-scale rearrangements of the atoms. In this letter we report a study of possible structures of  $C_6Ca$  under pressure, finding that large-scale atomic rearrangements are favoured at quite low pressures. We find that the behaviour of the  $C_6Yb$  shares a similar phenomenology.

Before discussing the methodology, let us first summarise the main findings. The results below reveal that the low enthalpy structures of  $C_6Ca$  (and other GICs) can be broadly classified into different classes. While the planar structure of  $C_6Ca$  is stable at ambient pressure, structures involving a buckling of the graphene sheets becomes energetically competitive over a range of intermediate pressures. At a comparatively low pressure of ca. 18 GPa, however, we find that the familiar honeycomb lattice structure of the graphene layers becomes unstable towards a rearrangement involving large- and small-diameter carbon rings, with the former accommodating the metal ion intercalate. With such an arrangement, the volume may be reduced without greatly increasing the internal energy, which results in a low enthalpy.

To arrive at these conclusions, we have carried out an extensive search within the “space of possible structures” of  $C_6Ca$  by relaxing a large number of random structures at a constant pressure of 15 GPa. (The general methodology parallels that described in Ref. [13].) This approach allows a search of the structure space with unbiased initial conditions. The calculations were performed within density functional theory [15] using the CASTEP package [14], with a plane wave basis set and ultrasoft pseudopotentials. To remain consistent with our previous work on the electronic structure of  $C_6Ca$  [4], we chose to use the local density approximation [16] for the exchange-correlation functional and used the pseudopo-

---

\*Present address: Department of Engineering, University of Cambridge, Trumpington Street, CB2 1PZ, United Kingdom

tentials that come with the CASTEP package, dividing the electrons into 2 core electrons and 4 valence electrons for C, 10 core and 10 valence for Ca, and 42 core and 28 valence for Yb. We tested the relative stability of the most stable structures with a generalised gradient approximation [17] and found no significant changes. The initial conditions for the geometry optimisations consisted of a unit cell containing one formula unit (7 atoms) with random atomic positions and random lattice vectors, the latter bounded so that the unit cell volume was within a factor of two of the ambient value. For the structure-space search we used a medium quality of plane wave cut-off energy (270 eV) and Brillouin zone integration ( $0.07 \text{ \AA}^{-1}$ ), so that the optimisations were fast, thus enabling a larger number of runs to be carried out using the available computing resources (32 processor Xeon cluster). The search is believed to be nearly exhaustive over the range of 7-atom cells because the low enthalpy structures came up repeatedly during the search. The *Pmma* structure with a 14-atom unit cell was built by hand using the intuition gained from the results of the random search.

As mentioned above, the search produced a number of novel structures which can, broadly, be grouped into two families. The first consists of the well-known rhombohedral or trigonal  $R\bar{3}m$  structure which is the stable low-pressure phase of  $C_6Ca$ , and its lower symmetry variants in which the bonding topology of the graphene sheets remains intact, but the sheets are buckled (see Fig. 1). In these buckled configurations, the Ca ions occupy the troughs between the buckled sheets, which results in a small reduction in overall volume. The principal difference between the *Cm* and the *C2/m* structures is that, in the former, the metal sheets are stacked in an  $\alpha\beta\gamma$  sequence, just as in the  $R\bar{3}m$  structure, whereas the latter has an  $\alpha\alpha$  stacking. Structures consisting of nano-porous carbon framework filled with Ca atoms were also found, but they were higher in enthalpy at these pressures.

Despite the buckling of the sheets, the integrity of the hexagonal carbon ring structure in this family of compounds is maintained. In the second family of low enthalpy compounds, the carbon and Ca atoms maintain a planar geometry, but the hexagonal ring structure is replaced by a network of different sized rings. The *Pmma* structure has five-, six- and seven-membered rings, whereas the *Cmmm* structure has only five- and eight-membered rings. A useful way to think about these bonding topologies is that they result from one (*Pmma*) or two (*Cmmm*) Stone-Wales (SW) bond rotations [18], starting from the regular hexagonal graphene network. The last two structures are reminiscent of those of a class of ternary boride compounds, whose prototype is  $YCrB_4$ . To our knowledge, its structure, consisting of metal ion layers and boron sheets with five- and seven-membered, was first proposed by Kuz'ma [19]. Several other mem-

Space group	Lattice parameters ( $\text{\AA}$ , $^\circ$ )			Atomic coordinates (fractional)		
<i>Cmmm</i>	$a=9.07$	$b=3.66$	$c=3.54$	C1	0.079	0.000
	$\alpha=90$	$\beta=90$	$\gamma=90$	C2	0.175	0.308
				Ca	0.500	0.000
$R\bar{3}m$	$a=4.24$	$b=4.24$	$c=12.28$	C	0.000	0.333
	$\alpha=90$	$\beta=90$	$\gamma=120$	Ca	0.000	0.000
<i>Pmma</i>	$a=4.82$	$b=3.74$	$c=6.7$	C1	0.250	0.500
	$\alpha=90$	$\beta=90$	$\gamma=90$	C2	0.514	0.500
				C3	0.750	0.500
				C4	0.596	0.500
				Ca	0.250	0.000
<i>C2/m</i>	$a=7.30$	$b=4.23$	$c=4.15$	C1	0.000	0.334
	$\alpha=90$	$\beta=102$	$\gamma=90$	C2	0.171	0.168
				Ca	0.000	0.000
<i>Cm</i>	$a=7.32$	$b=4.24$	$c=6.4$	C1	0.246	0.166
	$\alpha=90$	$\beta=105$	$\gamma=90$	C2	0.054	0.332
				C3	0.413	0.333
				Ca	0.531	0.500

TABLE I: Details of  $C_6Ca$  structures at 15 GPa, calculated at the higher level of precision.

bers of the class have since been identified [20, 21].

To further increase the accuracy of the procedure, we chose promising representative structures from the different families and refined them using a higher plane wave cut-off energy (480 eV) and Brillouin Zone sampling ( $0.05 \text{ \AA}^{-1}$ ). The converged lowest enthalpy structures obtained are defined in Table I. Figure 2 shows the enthalpies of the new structures, referenced to the  $R\bar{3}m$  structure, as a function of external pressure. The buckled *Cm* structure is slightly less stable than the  $R\bar{3}m$  structure at pressures up to about 18 GPa, but at higher pressures it becomes more favourable. In fact the  $R\bar{3}m$  and buckled structures are always close in enthalpy, and their relative stability cannot be conclusively asserted because of inherent systematic errors in the local density approximation (commonly estimated as 0.05 eV/atom for total energy differences). The *Pmma* and *Cmmm* structures show a steep decline in relative enthalpy, indicating that they would be favoured at high pressure. Considering the geometry of these structures, it can be seen that the energy cost of the SW bond rotations is offset by a significant reduction in volume (up to 20%), as the metal ions are accommodated within the larger rings. The enthalpy-pressure curve of *Pmma* has a lower slope than that of *Cmmm* because it involves one SW bond rotation rather than two, so that the rings in which the Ca atoms sit are smaller and the volume reduction is not as large.

Figure 3 shows the band structure corresponding to the *Cmmm* structure. Comparing it to that of the “empty” carbon skeleton (after removal of the metal ions), it can

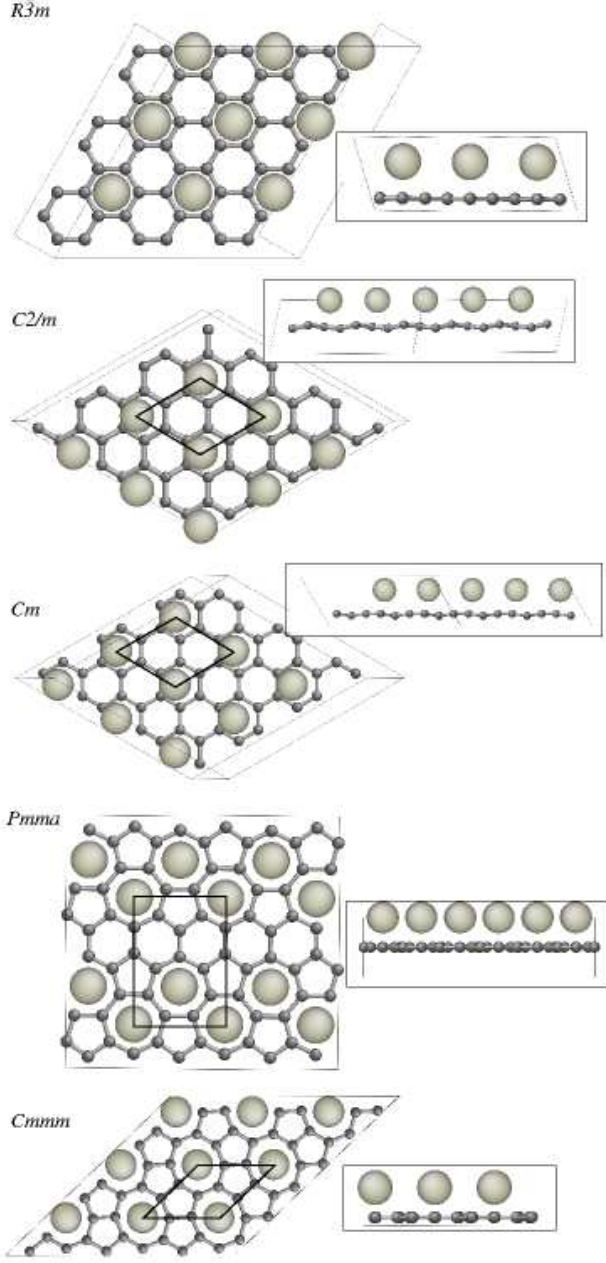


FIG. 1: Low enthalpy structures of  $C_6Ca$  found during the structure space search. The top panel shows the familiar  $R\bar{3}m$  structure, which is stable under ambient conditions. The Ca ions (large) are situated between the layers, occupying sites above the centres of the hexagonal rings in an  $\alpha\alpha$  stacking arrangement. The following two panels show lower symmetry variants, with  $C2/m$  and  $Cm$  structures, where in each case the graphene sheets are buckled (as depicted in the side views shown as insets) and the Ca ions are rearranged. While all of these buckled structures are energetically competitive, it is not possible to conclude from our calculations whether any become globally stable at intermediate pressures. The bottom panels show structures in which the hexagonal carbon rings of the graphene sheets are transformed, by a sequence of Stone-Wales bond rotations, into five-, six- and seven-membered ( $Pmma$ ) or five- and eight-membered rings ( $Cmmm$ ). At high enough pressure, the latter structure is expected to become globally stable.

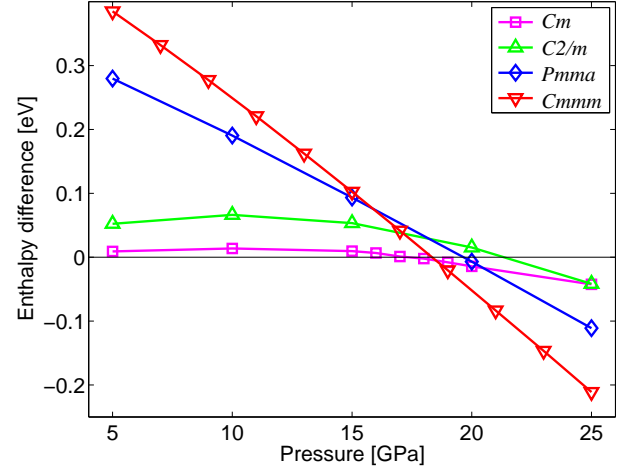


FIG. 2: The enthalpy differences per  $C_6Ca$  formula unit of our new structures, referenced to the  $R\bar{3}m$  structure.

be seen that, upon intercalation, a new dispersive band becomes occupied in much the same way as in the parent  $R\bar{3}m$  structure [4]. However, the density of states (DoS, shown in Figure 4) at the Fermi level is significantly lower (on both the Ca and C atoms) in the  $Cmmm$  structure, suggesting that the conditions for superconductivity are likely to be less favourable. In addition, the general shape of the DoS looks much less like that of graphite as compared with the  $R\bar{3}m$  structure.

Taken together, these findings present a coherent picture of the behaviour of  $C_6Ca$  under pressure. At low pressures, the graphene sheets remain flat, leading to the familiar  $R\bar{3}m$  structure. However, this parent structure is but one member of a larger family of compounds in which the integrity of the hexagonal rings is maintained, while the graphene sheets become buckled to accommodate Ca atoms within the troughs. The troughs allow more space for the Ca atoms, so these structures are favoured over  $R\bar{3}m$  at higher pressures, although the gain is limited. At still higher pressures, another more drastic solution emerges in which the bonding topology of the carbon atoms is disrupted by SW bond rotations within the graphene layer. A single SW bond rotation results in five-, six- and seven-membered rings, as in the  $Pmma$  structure, and two SW bond rotations result in five- and eight-membered rings as in the  $Cmmm$  structure. The SW mechanism results in large-diameter carbon rings, within which the Ca atoms sit, giving a substantial volume reduction, and these structures become stable at pressures above about 18 GPa. The accompanying phase transition is expected to be strongly first order, and the electronic structure of the large-diameter-ring structures is strongly modified from that of  $R\bar{3}m$ . In summary, and recalling the experimental evidence for a phase transition, we conclude that our simulations strongly predict a transition to the structure like  $Pmma$  or  $Cmmm$  at

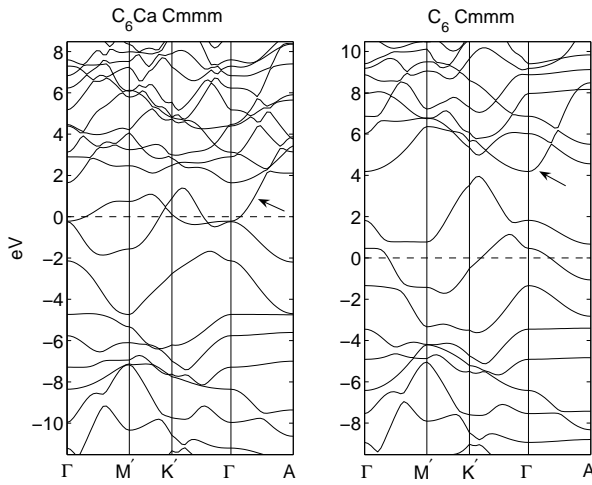


FIG. 3: The band structure of the  $Cmmm$  structure (left), and the corresponding “empty” structure with the metal ions removed (right). The two panels have been aligned vertically using the bottom of the sigma bands (not shown), the respective Fermi levels are indicated by dashed lines. Since the space group of this structure is almost hexagonal, we have used the corresponding notation for the points of high symmetry in the Brillouin Zone and indicated the small discrepancy by using primed letters. Note the increase in the Fermi level upon intercalation, accompanied by the lowering and subsequent occupation of the dispersive interlayer band (marked by an arrow).

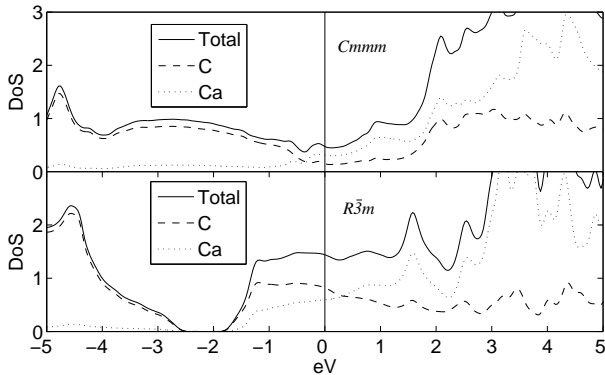


FIG. 4: Density of states, resolved into contributions on the C and Ca atoms, corresponding to the  $Cmmm$  (top) and  $R\bar{3}m$  (bottom) structures, calculated at 15 GPa.

sufficiently high pressures, but due to the intrinsic errors associated with DFT, it is uncertain whether the observed transition is this one. It is possible that one of the buckled structures becomes the most stable one for an intermediate range of pressure, in which case we predict a *second* phase transition at higher pressure.

Further calculations show that the bonding between the metal and carbon atoms is stronger than might be expected, and all the structures considered here are sta-

ble against phase separation into diamond/graphite and pure *fcc/bcc* Ca. We have also studied the stability of above phases of  $C_6Yb$  under pressure, and again we find that structures with Yb atoms sitting within larger membered rings are stable at pressures above about 18 GPa. We conjecture that the occurrence of such rings accommodating the intercalate atoms might be a general feature of graphite intercalation compounds under high pressures.

CJP was supported by an EPSRC Advanced Research Fellowship. We are grateful for G. Lonzarich for bringing to our attention the references on the ternary borides.

- 
- [1] M. S. Dresselhaus and G. Dresselhaus, Adv. in Phys. **51**, 1–186 (2002).
  - [2] T. Weller, M. Ellerby, S. S. Saxena, R. Smith, and N. Skipper, Nature Physics, **1** 39–41 (2005).
  - [3] N. Emery *et al.*, Phys. Rev. Lett. **95**, 087003 (2005).
  - [4] G. Csányi, P. B. Littlewood, A. H. Nevidomskyy, C. J. Pickard, and B. D. Simons, Nature Physics, **1** 42–45 (2005).
  - [5] R. A. Jishi and M. S. Dresselhaus, Phys. Rev. B **45**, 12465 (1992).
  - [6] M. Calandra and F. Mauri, Phys. Rev. Lett. **95**, 237002 (2005).
  - [7] I. I. Mazin, Phys. Rev. Lett. **95**, 227001 (2005).
  - [8] I. I. Mazin *et al.*, cond-mat/0606404.
  - [9] A. Gauzzi *et al.*, cond-mat/0603443.
  - [10] R. P. Smith *et al.*, cond-mat/0604204.
  - [11] J. S. Kim *et al.*, cond-mat/0603530.
  - [12] M. Calandra and F. Mauri, cond-mat/0606372.
  - [13] C. J. Pickard and R. J. Needs, Phys. Rev. Lett. **97**, 045504 (2006).
  - [14] S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. J. Probert, K. Refson, and M. C. Payne, Zeitschrift für Kristallographie **220** 567–570 (2005).
  - [15] M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, Rev. Mod. Phys. **64**, 1045–1097 (1992).
  - [16] J. Perdew and A. Zunger, Phys. Rev. B **23**, 5048–5079 (1981).
  - [17] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
  - [18] A. J. Stone and D. J. Wales, Chem. Phys. Lett. **128**, 501 (1986).
  - [19] Yu. B. Kuz’ma, Sov. Phys. Crystallogr. **15**, 312–314 (1970).
  - [20] Z. Fisk, K. N. Yang, M. B. Maple, and H. R. Ott, in Valence Fluctuations in Solids, eds: L. M. Falicov, W. Hanke, M. P. Maple, North-Holland Publishing Company: New York, 1981, pp. 345–347.
  - [21] H. F. Braun and K. Yvon, Acta Cryst. B **36**, 2400–2402 (1980).
  - [22] Note that such behaviour seems incompatible with the development of staging structures.